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Ordering potential – the anomalous structure and properties of liquid LiNa alloy

P P Nath, S Sarkar and R N Joarder*
Department of Physics, Jadavpur University, Kolkata-700 032, India
E-mail : rnj@juphys.ernet.in

Abstract : Using pseudopotential theory the *ab initio* calculation for ordering potential of liquid LiNa alloy is presented. Taking into account the electronic charge transfer and also charge neutrality condition we find the effective valencies in the alloy. We then use the model to obtain the Bhatia-Thornton structure factors, particularly at null alloy concentration (L_I = 0.61). The calculations of concentration fluctuation and other related thermodynamic properties show that this ordering potential approach works reasonably for this phase-separating (ps) liquid alloy system.

Keywords : Ordering potential, structure, liquid alloy.

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1. Introduction

In literature, both phase separating (ps) and compound forming (cf) liquid alloys have been discussed in terms of Yukawa tails between unlike pairs, repulsive for ps alloys while attractive for cf alloys [1]. Though the size effects are important in alloy behaviour, the nature of the interaction at the nearest neighbour dissimilar pairs play the major role. This can be shown through the *ab initio* calculation of the ordering potential constructed from the interionic forces in the alloy modified by charge transfer effects [2]. In this presentation we show the anomalous structural properties of liquid LiNa alloy as a function of Li concentration. To stress its distinctive properties from a typical cf liquid alloy KPb we show some results for KPb alloy as well.

2. Effective pair potential (epp) and ordering potential

The ordering potential is related to concentration–concentration correlation function and can be expressed in q-space by [1]

$$Vcc(q) = 4\ \pi\Delta z^2\ e^2/q^2 - q^2/4\ \pi e^2\ (1 - 1/\varepsilon(q)) .[\Delta u(q)]^2, \quad (1)$$

where $\Delta z = z_1 - z_2$, the difference in effective valencies of the two species.

$\Delta u = u_1 - u_2$, the difference in electron–ion pseudopotentials of the two species, $\varepsilon(q)$, the dielectric function of the alloy. The concentrations c_1 and c_2 of the two species govern z_1, z_2 and $\varepsilon(q)$ and hence $Vcc(q)$.

The effective valencies in the alloy are obtained using charge neutrality condition and charge transfer effects assumed to be maximum at the stoichiometric concentration [2]. $Vcc(r)$ is obtained by

$$Vcc(r) = 1/(2\ \pi)^3 \rho \int Vcc(q) e^{iqr} dq, \quad (2)$$

and it is related to the interchange or order energy parameter W, [1] (for substitutional model) given by

$$W = \rho \int Vcc(r) g(r) dr. \quad (3)$$

where $g(r)$ is the pair distribution function (PDF) of the system.

As is well known W controls the alloy behaviour [1].

3. Structural properties

The Bhatia–Thornton (BT) partial structure factors are most useful indicators of the alloy behaviour. In terms of q-space direct correlation function (dcf), $c_{\alpha\beta}(q)$ one can obtain [3] the partial structure factors, number-number,

*Corresponding Author

$S_{NN}(q)$, number–concentration, $S_{NC}(q)$, concentration–concentration, $S_{CC}(q)$ given by

$$S_{NN}(q) = \Theta(q) + \Delta^2(q)\, S_{CC}(q), \tag{4a}$$

$$S_{NC}(q) = -\Delta(q)\, S_{CC}(q), \tag{4b}$$

$$S_{CC}(q) = c_1c_2/(1 - c_1c_2\rho\{[c_{11}(q) + c_{22}(q) - 2c_{12}(q)] + \Delta^2(q)\Theta^{-1}(q)\}), \tag{4c}$$

where

$$\Theta(q) = \{1 - \rho[c_1^2c_{11}(q) + c_2^2c_{22}(q) - 2c_1c_2c_{12}(q)]\}^{-1} \tag{5a}$$

and

$$\Delta(q) = \rho\Theta(q)\{c_1[c_{11}(q) - c_{12}(q)] - c_2\,[c_{22}(q) - c_{12}(q)]\}. \tag{5b}$$

The total X-ray or neutron structure factor $S(q)$ is given by

$$S(q) = \{\langle f\rangle^2 S_{NN}(q) + 2\langle f\rangle(f_1 - f_2)S_{NC}(q) + (f_1 - f_2)^2\, S_{CC}(q)\}/\langle f^2\rangle,$$

where, terms have their usual meaning [2].

The calculation is carried out in (O)RPA (optimum random phase approximation) [2] where *epp* is separated into a reference part and a tail part. The reference part is replaced by a HS-(hard sphere) system of appropriate core diameter as per WCA (Weeks-Chandler-Andersen)–type criterion approximated by [4]

$$V_\alpha(\sigma_\alpha^{WCA}) - V_\alpha^{\min} \equiv K_BT \tag{6}$$

with $\alpha = 1$ and 2.

The FT (Fourier transform) of the tail part in the NFE (nearly free electron) model using linear response theory for the screening is obtainable based on appropriate pseudopotentials [2]. Equivalently, one can obtain similar results (but not in details) by considering Yukawa type interaction between 1-2 pairs [2].

4. Results

In Figure 1, we show the ordering potentials for liquid LiNa and KPb alloys at stoichiometric concentrations. Evidently the characteristic interaction in the nearest 1-2 pair at the nearest neighbor distance is opposite. The experimental ordering potential for liquid LiNa alloy was obtained [5] from an approximate relationship for null alloy composition (which is also the stoichiometric concentration) and evidently possesses some features exhibited by calculated one.

In Figure 2(i), we show the structural results for liquid LiNa alloy at three different Li concentrations (c_1)

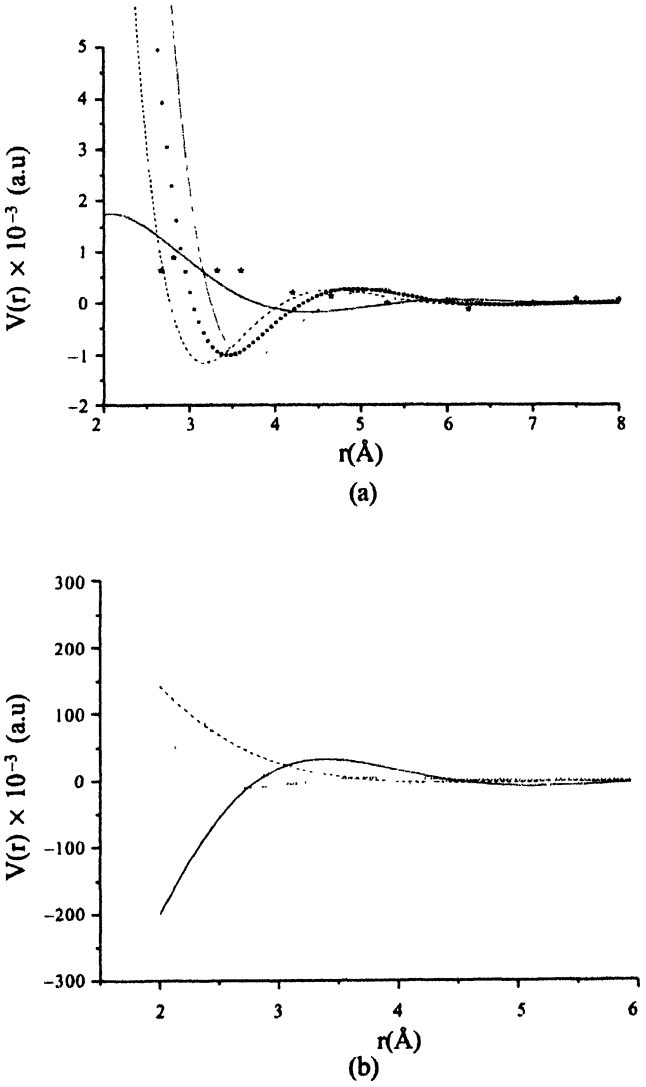
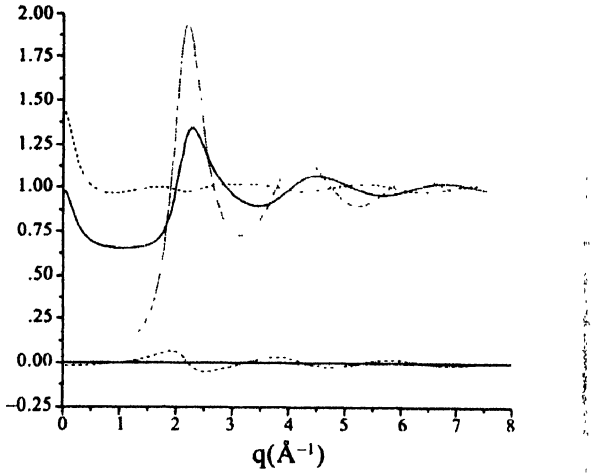
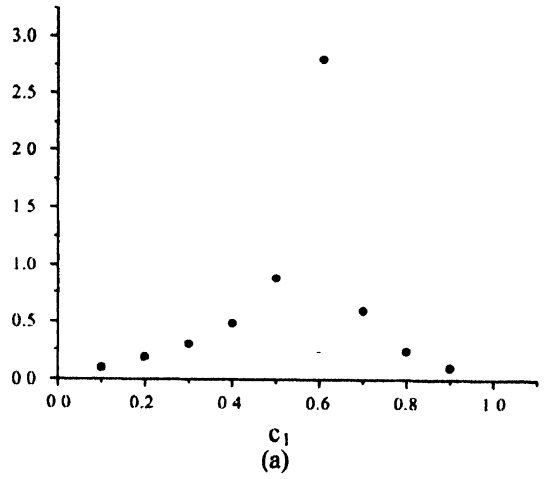
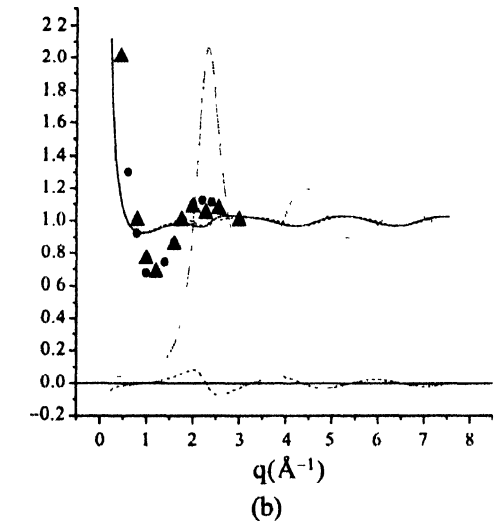


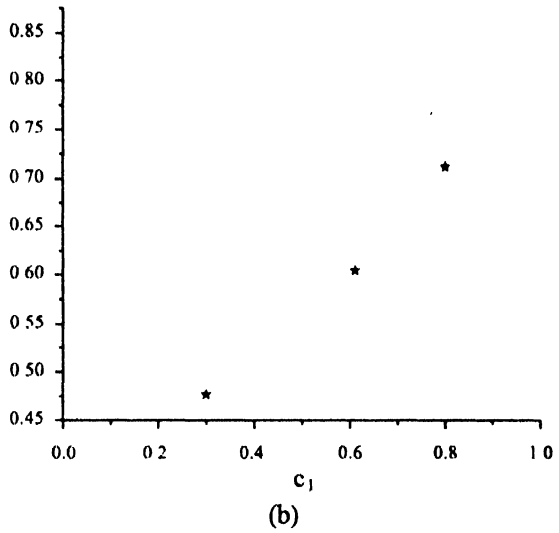
Figure 1. Ordering potential and atom-atom *epp* with subscript one for Li/K at stiochiometric concentration : (a) LiNa (b) KPb. $V_{cc}(r)$___, $V_1(r)$____, $V_2(r)$ ---, $V_{12}(r)$ ..., $V_{cc}(r)$, Exptl. [5] * * * *.

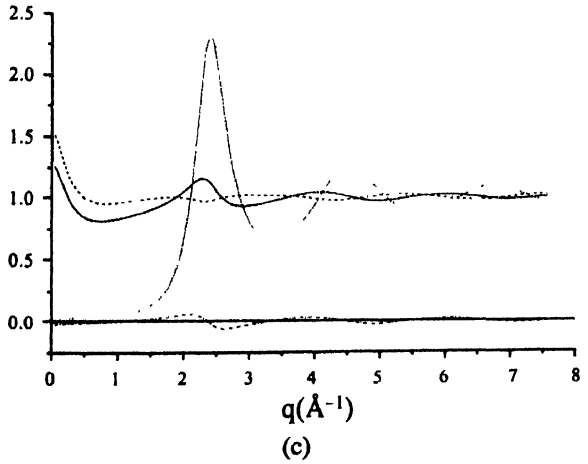
with one at null alloy concentration (Figure 2(ib)). $S_{CC}(q)$ shoots up as $q/0$ and does so drastically for null alloy composition showing strongest concentration fluctuation and phase separating tendency for the alloy. The experimental data of Ruppersberg and Knoll [5] and HS Yukawa model calculations of Ginoza [6] for null alloy composition are shown for comparison. Though the agreement between experimental data and the calculated one up to $q \sim 3$Å^{-1} in regard to the magnitude is lacking the important basic features, namely, $S_{CC}(q)$ drastically shoots up as $q/0$ and the double peak in the region $q \sim$ 2–3 Å^{-1} are produced quite well. Ginoza's calculation though











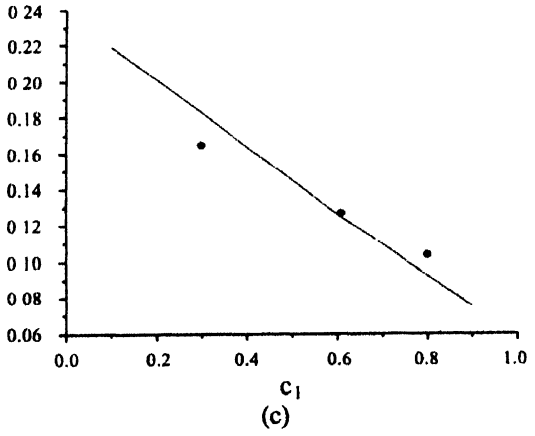
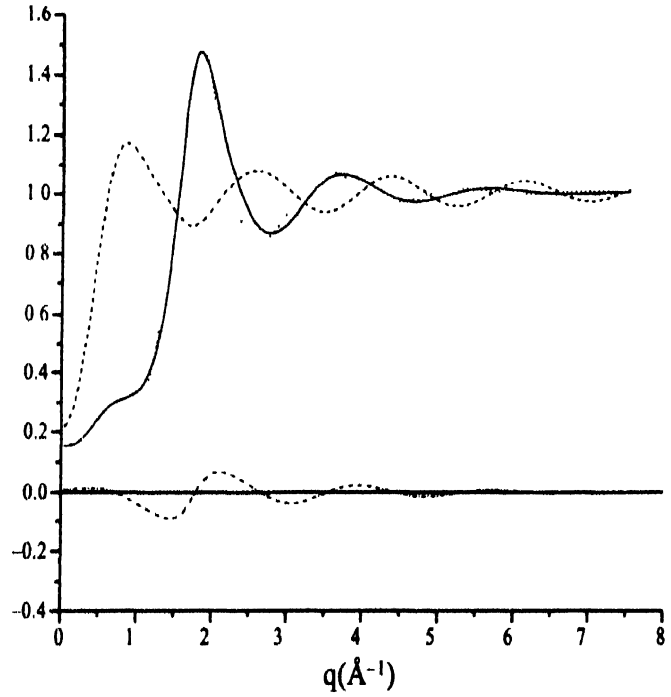


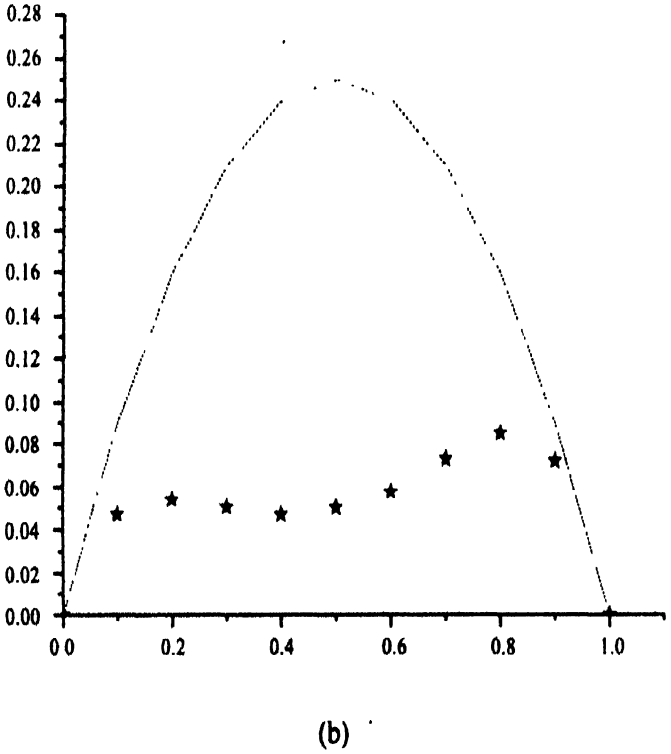
Figure 2(i). LiNa liquid alloy, structure factors *vs* q : $S(q)$_____, $S_{NN}(q)$ - - - , $S_{NC}(q)$ -.- .- , $S_{CC}(q)/c_1c_2$ _ _ _ at (a) $c_1 = 0.3$, (b) c_1=0.61 (null alloy) and (c) c_1=0.8 . Exptl. [5]▲▲▲, HS Yukawa model [6] • • •.

Figure 2(ii). LiNa liquid alloy, thermodynamic properties *vs* c_1 : (a) $S_{CC}(0)$, calcd. • • •, ideal - - - (b) Δ (0), calcd. - - -, observed * * * $(c)\chi_T$, calcd.____, by linear interpolation of pure comp. data • • • •.

agrees with experimental data very well up to q ~2 Å^{-1} could not produce the important double peak feature.



(a)



(b)

Figure 3. KPb liquid alloy, (a) structure factors *vs* q at K-conc., $c_1 = 0.5$, $S(q)$____, $S_{CC}(q)/c_1c_2$ _ _ _ , $S_{NN}(q)$ - - - -, $S_{NC}(q)$ -.-.-. (b) $S_{CC}(0)$ *vs* c_1 calcd.* * *, ideal - - - .

In Figure 2(iia), we show the variation of $S_{CC}(0)$, the long wave limit of the concentration-concentration structure factor ($=N\langle\Delta c^2\rangle$, where $\langle\Delta c^2\rangle$ is the mean square fluctuation) of liquid LiNa as a function of Li concentration c_1. The comparison of calculated data with ideal ones shows that the concentration fluctuation is exhibited strongly indicating phase separating behaviour. To our knowledge, no experimental measurement of $S_{CC}(0)$ as a function of component-concentration is available. The other thermodynamic functions like the volume change $\Delta(0)$ ($= 1/V(\delta V/\delta c_2)_{N,T,P}$) and the isothermal compressibility χ_T (obtained from $\theta(0) = \rho K_B T \chi_T$) are also shown as functions of Li concentration. The agreement for volume change with the observed data is reasonable. For χ_T, the deviation from the ideal behaviour is evident.

In Figure 3, we show some similar results for liquid KPb alloy. The behaviour is evidently opposite. There is a pre-peak formation in the total structure factor $S(q)$ corresponding to an enhanced $S_{CC}(q)$ peak at that q-value. This pre-peak has the indication of the existence of strong chemical short range ordering [7].

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